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Synthesis of 1,6-Diaminodiamantane

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Abstract: A new polycyclic diamine, 1,6-diaminodiamantane, was synthesized starting from 1,6dibromodiamantane. The reaction of 1,6-dibromodiamantane with acetonitrile using H2SO4 as catalyst afforded 1,6-diacetamidodiamantane in 72% yield. The reaction of 1,6-diacetamidodiamantane with NaOH afforded 1,6-diaminodiamantane in 50% yield.

Diamantane is a cycloaliphatic cage hydrocarbon containing an "extended cage" adamantane structure.¹ Although diamantane has been of interest to synthetic chemists for many years,¹ its use in polymers is limited. There is only one report indicating that the thermosetting resins prepared from diethynyl diamantane are stable at 518°C in air.² It is noteworthy that intermolecular charge-transfer complexes are formed between imide and amine moieties for the usual polyimides composed of aromatic diacid anhydrides and aromatic diamines.³ The formation of intermolecular charge-transfer complexes would be the reason for the coloration and the high dielectric constansts of polyimides compared to other polymer films. In order to eliminate the influence of charge transfer, polyimides with alicyclic diamines have been prepared recently.⁴ Although Smith *et al.* have reported the synthesis of 1,3-diaminoadamantane, the synthetic route involves two high pressure steps.⁵ Moreover, 1,3-diaminoadamantane is unstable in the atmosphere.⁵ The present work relates the facile synthesis of two novel compounds, 1,6-diacetamidodiamantane (1) and 1,6-diaminodiamantane (2) from 1,6dibromodiamantane following a known procedure.^{1b,1d}

The synthetic route to the compounds 1 and 2 is illustrated in Scheme 1. All products were fully characterized spectroscopically (2D, ¹H- and ¹³C-NMR). The reaction of 3 with acetonitrile in the presence of H2SO4 afforded 1 in 72% yield.⁶ The reaction of 1 with NaOH afforded compound 2 in 50% yield.⁷ Water was added to dilute the reaction mixture after reflux,⁷ and the quantity of the water would affect the efficiency of extraction of the diamine 2. The structure was confirmed unambiguously by a single-crystal X-ray analysis of 2^7 and the ORTEP diagram is shown in Figure 1. The diamine 2 is stable in the atmosphere.

We also attempted to prepare 1,3-diaminoadamantane from 1,3-dibromoadamantane by the same procedure as for synthesizing the diamine 2. But 1,3-diacetamidoadamantane was obtained in trace, probably due to the low reactivity of 1,3-dibromoadamantane. Studies on the preparation of polyamides and polyimides from 2 will be reported elsewhere in the near future. Antitumor and antimicrobial activities of 2 will be reported elsewhere.



Scheme 1



Figure 1. ORTEP diagram of 2

References and Notes

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- 6.1,6-Diacetamidodiamantane (1): Compound 3 (0.043 mol) was dissolved in a mixture of cyclohexane (100 ml) and acetonitrile (132 ml), and H₂SO₄ (97%, 6 ml) was added with stirring. Stirring was continued at 38 °C. After 16 hours, water and ice were added to the stirring mixture (a thick orange suspension). The white precipitate thus formed was purified (filtered and washed), and 11.1 g of white powder was obtained after recrystallization from acetone to give 1 in 72% yield. Compound 1 : mp 400 °C ; IR(KBr) 3292,2918,2871,1651,1556,1366 cm⁻¹; EIMS m/z(%) 302(M⁴,100), 287(26), 259(2), 243(80); ¹H NMR(300 MHz, DMSO-d6) δ 1.30(4H,m J=12.2 Hz, H-3a,8a,10a,14a), 1.77(6H, s, CH3), 1.84(6H, m, H-4,5.9,13), 1.92(4H, m, J=12.9 Hz, H-3b, 8b, 10b, 14b), 2.38(4H, s, H-2,7,11,12), 7.13(2H, s, NH); ¹³C NMR(75 MHz, DMSO-d6) δ 23.60(CH3) , 27.20(C-4,9), 31.60(C-3,8,10,14), 38.49(C-2,7,11,12), 41.39 (C-5,13), 54.34(C-1,6), 168.48(CO).
- 7.1,6-Diaminodiamantane(2): Compound 1 (36.4 mmol) was refluxed for 24 hours in diethylene glycol(220 ml) solution of NaOH (23.5 g). The reaction mixture changed to yellow and then to orange-brown, and was then diluted with water (750 ml). The normal work up of the product produced white crystals of compound 2 in 50% yield after vacuum sublimation. The single crystal of 2 grew from the diamine 2 in benzene. Compound 2: mp 324°C; IR(KBr) 3352, 3279, 3163, 2888, 2867, 1594, 1167 cm⁻¹; EIMS m/z(%) 218(M⁺, 80), 201(100), 186(16); ¹H NMR(300 MHz, C6D6) δ 0.75(4H, s, NH2,disappear by D2O), 1.25(4H, m, J=13.1 Hz, H-3a,8a,10a,14a), 1.35(8H, m, H-2,5, 7,11,12,13), 1.79(2H, s, H-4,9), 2.10(4H, m, J=12.8 Hz, H-3b, 8b, 10b, 14b); ¹³C NMR(75 MHz, C6D6) δ 29.38(C-4,9), 32.53(C-3,8,10,14), 45.16(C-2,7,11,12), 48.04(C-5,13), 49.84(C-1,6); Crystal data: C14H22N2, colorless crystal, 0.40 × 0.50 × 0.60 mm, tetragonal, P 42bc with a=15.633 (6), c=9.484 (3) Å with Dc=1.251 gcm⁻³ for Z=8, V=2317.7 (11) Å³, T=298 K, $\lambda = 0.17.7$ Å, $\mu = 0.690$ cm⁻¹, F(000)=960, Rw=0.033 for 803 observed reflections. Atomic coordinates and full details of molecular dimensions have been deposited to the Cambridge Crystallographic Data Centre.

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